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Emerging and legacy flame retardants in UK indoor air and dust: evidence for replacement of PBDEs by emerging flame retardants?

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Abstract

Concentrations of 27 emerging (EFRs) and legacy flame retardants (LFRs) were measured in samples of indoor air (n=35) and indoor dust (n=77) from UK homes and offices. All target compounds were detected in indoor air and dust samples. Relatively volatile EFRs (e.g. tetrabromoethylcyclohexane – DBE-DBCH) were more frequently detected in indoor air (detection frequencies > 60%), while less volatile EFRs (e.g. tetrabromobisphenolA-bis(2,3-dibromopropyl ether (TBBPA-BDBPE) and decabromodiphenyl ethane (DBDPE)) were predominant in dust. Concentrations of some EFRs (e.g. DBDPE) exceeded significantly those reported previously in UK dust ($p<0.05$), while concentrations of BDE-209 in office dust were significantly lower ($p<0.05$) than those reported previously in UK offices, consistent with the application of DBDPE as an alternative to the Deca-BDE formulation, of which BDE-209 is the principal constituent. Moreover, concentrations of BDEs 47 and 99 (both major constituents of the Penta-BDE product) in office air were significantly lower ($p<0.05$) than those in previous UK studies. Our results constitute important early evidence that restrictions on PBDEs have increased demand for EFRs in the UK, with the result that human exposure to PBDEs in UK homes and offices has decreased while exposure to EFRs has risen.

Introduction

Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) were among the most extensively used brominated flame retardants (FRs) up to 2004.[1,2] Since then, the Penta-BDE and Octa-BDE commercial mixtures have been listed under the Stockholm Convention on Persistent Organic Pollutants (POPs)[3] and production and use of both commercial mixtures phased out in Europe and North America.[4] Additionally, use of Deca-BDE in the EU has been banned in electrical and electronic applications since 1 July 2008[5], and it is currently slated for listing under the Stockholm Convention. Moreover, HBCDD has also been listed as a POP under the same convention.[6] Following these bans and restrictions on PBDEs and HBCDD (collectively referred to as "legacy" flame retardants - LFRs), without concomitant relaxation of flame retardancy regulations, there is potential for these products to be replaced by so-called "emerging" flame retardants – EFRs – whose use is not restricted but that possess chemical structures similar to those of LFRs.[1,7] While this similarity is advantageous in the context of their ability to impart flame retardancy; there are concerns it extends to their toxicity and adverse environmental behavior – e.g. persistence and capacity for bioaccumulation.

While knowledge of environmental contamination with EFRs remains scant compared to our understanding of LFRs like PBDEs; recent reports show a broad suite of EFRs including DBDPE, 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), bis(2-ethylhexyl)-tetrabromophthalate (BEH-TEBP), dechlorane plus (DDC-CO) and TBBPA-BDBPE to be present in indoor dust from various countries including the USA[8], China[9], Sweden[10], Germany[11], Belgium[12] and the UK[13]. In a previous UK study, BTBPE and DBDPE were detected in both office and home dust.[13] However, very little is known about concentrations of EFRs in indoor air. DBE-DBCH, pentabromotoluene (PBT), and hexabromobenzene (HBB)

were detected frequently in Swedish indoor air[14], while Cequier et al.[15] also found DBE-DBCH, PBT, HBB, DBDPE and pentabromobenzene (PBBz) in most indoor air samples from Norwegian households and primary schools.

EFRs like DBE-DBCH, BTBPE, DBDPE and DDC-CO display potential for persistence and bioaccumulation that exacerbates concern over their adverse human health effects.[16–22] Moreover, animal studies suggest some EFRs pose health risks including: endocrine disruption (DBDPE, BTBPE, EH-TBB, BEH-TEBP and DBE-DBCH), neurodevelopmental and behavioural effects (EH-TBB, BEH-TEBP), hepatotoxicity (DBDPE), impaired reproductive physiology (DBDPE and DBE-DBCH), and gene expression (BTBPE); along with morphological abnormalities and mortality (DBE-DBCH), DNA damage (EH-TBB, BEH-TEBP and DBE-DBCH) and possibly cancer (DBE-DBCH).[22–35]

This study measured 16 EFRs, 8 PBDEs, and 3 HBCDD diastereomers in indoor air and settled floor dust from UK homes and offices. Concentrations of EFRs and LFRs were compared with those in previous UK studies to evaluate whether restrictions on PBDEs and HBCDD have reduced concentrations in indoor environments. Moreover, given that unlike other EU member states, the UK has – since 1988 - flame retardancy regulations that apply to furniture and furnishings, we compared our concentrations of target FRs with those reported from other countries. In addition, we estimated exposure to our target FRs via inhalation and dust ingestion by UK adults and toddlers.

Materials and Methods

Sample collection

Air samples were collected from February to May 2015 in offices (n=20) and houses (n=15) in

Birmingham, UK using double-bowl passive air samplers containing a polyurethane foam disk (PUF) and a glass fiber filter (GFF) (further information in the Supporting Information (SI) section). Each sampler was deployed for ~45 days at a height of 1-2 m.[36] Sampling rates (m^3/day) for PBDEs, HBCDDs and EFRs were derived from previously reported studies,[36–38] with detailed information provided as SI. In summary, the air sampling rates used were: a uniform value of 1.677 m^3/day for EFRs, and 1.74, 1.472, 0.992, 1.014, 0.685, 0.691, 0.55, 0.567, 0.807, 0.775, and 0.761 m^3/day for BDEs-47, 99, 100, 153, 154, 183, and 209, plus α-, β-, and γ-HBCDD respectively.

Dust was collected in offices (n=42) and houses (n=30) between June 2013 and May 2015. Samples were collected using a standard protocol under normal office and house use conditions to reflect actual human exposure.[13] (detailed information provided as SI). All dust samples were sieved through a pre-cleaned 500 μm mesh sieve, homogenized thoroughly, transferred to clean glass vials and stored at -20 °C until analysis. Details of the sampling methods are provided as SI.

Analytical protocols

Samples were spiked with internal standards (^{13}C-BDE 209, ^{13}C-BTBPE, ^{13}C-BEH-TEBP, BDE 77, BDE 128) before extraction. Air samples (combined PUF and GFF) and aliquots of dust samples (typically between 50 and 200 mg) were extracted with hexane/acetone (3:1, v/v) using pressurized liquid extraction (Dionex, ASE 350). Crude extracts were purified by washing with 3-4 mL concentrated sulfuric acid before reconstitution in 200 μL (dust) and 50 μL (air) iso-octane containing 250 pg/uL PCB-129 as recovery determination standard for quality assurance/quality control (QA/QC) purposes.

FRs were analyzed on a Trace 1310 gas chromatograph coupled to an ISQ™ single quadrupole

mass spectrometer (Thermo Scientific, TX, USA) operated in electron capture negative ionization (ECNI) mode. Two μL of cleaned extract were injected onto a Thermo Scientific TraceGOLD (TG)- Standard Quality Control (SQC) column (15 m×0.25 mm×0.25 μm) using a programmable-temperature vaporizer injector in solvent vent mode.[39] After gas chromatography/mass spectrometry(MS) analysis, samples were evaporated and reconstituted in 200 uL of methanol containing d_{18}-γ-HBCDD (25 pg/μL) as recovery determination standard for determination of HBCDDs by liquid chromatography (LC)-MS/MS.[40] Quality assurance included method and field blanks. Five-point calibration curves were constructed for each target compound with excellent linearity (R^2 >0.99) over a concentration range relevant to those in samples. Average internal standard recoveries were: 113±17% (BDE-77), 115±15% (BDE-128), 98±21% (^{13}C-BEH-TEBP), 108±27% (^{13}C-BTBPE), and 95±28% (^{13}C-BDE-209). Method accuracy and precision were evaluated via replicate analyses (n=6) of NIST SRM 2585 (organics in indoor dust). Detailed description of analytical methods and QA/QC measurements is provided as SI.

Statistical Analysis

Statistical analysis was conducted using Excel (Microsoft Office 2010) and IBM SPSS Statistics 21.0 (Chicago, IL, U.S.A.). Independent t-tests and ANOVA analyses were only conducted for target compounds with detection frequencies ≥ 60%. Where analyte peaks <LOQ, concentrations of target compounds were assumed to equal LOQ/2. Statistical analysis was performed on log-transformed concentrations, as concentrations in all data sets were revealed to be log-normally distributed using Kolmogorov-Smirnov test and visual inspection of quantile-by-quantile graphic plots. A *p*-value <0.05 was considered significant.

Results and discussion

Levels of FRs in indoor air

All target FRs were detected in indoor air from UK homes and offices (Table 1).

EFRs

In both homes and offices, more volatile EFRs (DBE-DBCH, PBBz, PBT, HBB, tetrabromo-*o*-chlorotoluene (TBCT), 1,2,4,5-tetrabromo-3,6-dimethylbenzene (TBX), pentabromoethylbenzene (PBEB), and 2,3-dibromopropyl 2,4,6-tribromophenyl ether (TBP-DBPE)) showed higher detection frequencies in air (DF > 60%), while the less volatile DDC-CO and TBBPA-BDBPE were only detected in <20% of samples (Table 1). This is likely attributable to greater indoor use of these chemicals coupled with their relatively higher vapor pressures and lower K_{OA} values (Table S3). The most abundant compounds in air were α- and β-DBE-DBCH, which when summed as ΣDBE-DBCH account for 63% and 80% of ΣEFRs in home and office air respectively. Median concentrations of ΣDBE-DBCH in home and office air were 110 and 290 pg/m^3 respectively, which exceeds slightly those reported in Norwegian households (77.9 pg/m^3), classrooms (46.6 pg/m^3)[15] and in Swedish indoor microenvironments (55 pg/m^3).[14] We are aware of only one commercial DBE-DBCH formulation (Saytex BCL-462), which contains equal amounts of the two diastereomers, α- and β-DBE-DBCH.[41] The ratio of β- to α-DBE-DBCH ($f_{\beta\text{-DBE-DBCH}}$) here ranged from 0.5 to 1.0, with a median value of 0.7, which is lower than in the commercial product. This is the first report of $f_{\beta\text{-DBE-DBCH}}$ in indoor air, which precludes comparison to other studies. Possible explanations for the different isomer distribution in air compared to the commercial product include: differences in physicochemical properties (e.g. vapour pressure) or atmospheric degradation between the two diastereomers and possible

143 isomerisation post-emission. The latter explanation appears unlikely, as thermal conversion of
144 the DBE-DBCH isomers occurs ≥125 ˚C.[41] However, such high temperatures could occur during
145 incorporation of DBE-DBCH into polymers. Consequently, $f_{\beta\text{-DBE-DBCH}}$ values in indoor air in this
146 study may reflect the pattern present in DBE-DBCH-treated items rather than that in the
147 commercial formulation.

148 Other frequently detected EFRs in air were: EH-TBB, BEH-TEBP and BTBPE. EH-TBB and
149 BEH-TEBP were major constituents of Firemaster 550 and Firemaster BZ-54.[42] BEH-TEBP was
150 also used in the flame retardant DP-45[42] and as a plasticizer in polyvinyl chloride and
151 neoprene.[43] The fraction of EH-TBB $f_{EH\text{-}TBB}$ = EH-TBB/(EH-TBB+BEHTBP). The $f_{EH\text{-}TBB}$ value
152 was 0.77 ± 0.03 in Firemaster 550 and 0.70 in Firemaster BZ-54.[43] The values of $f_{EH\text{-}TBB}$ in
153 indoor air here are 0.03-0.99 (median=0.64) which is comparable to those reported in indoor air
154 from Canada (0.3-0.99; median=0.83)[44], the USA (0.16-0.95; median=0.63)[44] and the Czech
155 Republic (0.27-0.89; median=0.72)[44] and outdoor air from Toronto, Canada (0.69)[45] and Chicago,
156 the USA (0.70)[46] but higher than outdoor air from the Great Lakes area (0.26-0.54)[42] and
157 Canada's Western Sub-Arctic (0.48)[47]. Such variation in $f_{EH\text{-}TBB}$ ratios between studies may be
158 attributable to different applications of BEH-TEBP across jurisdictions.

159 DFs of BTBPE, EH-TBB and BEH-TEBP exceed 70% in both microenvironment categories in
160 this study (Table 1). This exceeded DFs (>33%, with BTBPE not detected at all) for the same
161 compounds in Norwegian and Swedish air).[14,15] This apparent greater detection of these EFRs in
162 UK indoor air is at least partly attributable to the lower limits of quantitation (LOQs) in our
163 study (BTBPE, EH-TBB and BEH-TEBP were 1.0, 0.1 and 0.1 pg/m^3) compared to the
164 Scandinavian studies for which LOQs for BTBPE, EH-TBB and BEH-TEBP were 31, 330 and
165 35 pg/m^3 in the Swedish study and 15.7, 7.4 and 2.9 pg/m^3 in the Norwegian study.[14,15] While no

production information is available for the UK or the EU, both EH-TBB and BEH-TEBP are reported replacements for Penta-BDE, and BTBPE a replacement for Octa-BDE.[7] It is therefore possible that following phase out of LFRs, these EFRs were more widely used in the UK than Norway and Sweden as a result of the UK's 1988 Furniture and Furnishings (Fire) (Safety) Regulations that differ substantially from those elsewhere in Europe.[48]

PBDEs

BDEs-28, 47, 100, 99, and 209 were more frequently detected (DFs >85%) than other PBDEs (Table 1). Concentrations of ∑PBDEs (defined as the sum of PBDEs-28, 47, 100, 99, 154, 153, 183 and 209) were 36-6400 pg/m^3 (median=280 pg/m^3) in UK homes. Notwithstanding slight differences in the congeners constituting ΣPBDEs in different studies, the range of ΣPBDE concentrations reported here, is comparable to studies conducted in the USA (210-3980 pg/m^3) and Sweden (72-1400 pg/m^3), but higher than Germany (8.24-47 pg/m^3), Australia (0.5-179 pg/m^3) and Japan (17-55 pg/m^3)[49-53]. Concentrations of ∑PBDEs were 22-600 pg/m^3 (median=54 pg/m^3) in UK offices, similar to Australia (15-487 pg/m^3) but much lower than USA (21-17200 pg/m^3) and Sweden (140-7300 pg/m^3)[49–54]. BDE-209 predominated in homes and offices, contributing 73% and 50% of the total atmospheric PBDEs, respectively. This dominance of BDE-209 matches broadly that in Sweden[50], Germany[51], Australia[52], and Japan[53]. In contrast, BDE-47 and BDE-99 predominated in USA homes[49] and offices[54]. This different pattern in the USA is likely due the far more extensive use of Penta-BDE in USA (94.7% of global Penta-BDE demand) than other countries[55].

HBCDDs

In homes, concentrations of ∑HBCDDs were 19-1500 pg/m^3 (median=110 pg/m^3), comparable

188 to previously reported concentrations in UK houses (67-1300 pg/m^3; median=180 pg/m^3).[56] By
189 comparison, ∑HBCDDs in our offices (median=41 pg/m^3) were lower than those reported
190 previously in UK offices (median=170 pg/m^3).[56] Elsewhere, concentrations of ∑HBCDDs in
191 offices, apartments, stores and two schools in Sweden (<1.3-19 pg/m^3)[14] were exceeded
192 substantially by those reported here. On average, the HBCDD isomer distribution was 87% γ-
193 HBCDD, 8% α-HBCDD, and 5% β-HBCDD in homes, and 71% γ-HBCDD, 18% α-HBCDD,
194 and 11% β-HBCD in offices. This pattern is similar to previous reports for UK and Swedish
195 indoor air[14,56].

196 *Relative abundance of FRs in indoor air*

197 PBDEs predominated in homes, contributing 44% ΣFRs, while EFRs predominated in offices,
198 accounting for 83% ∑FRs. ∑HBCDDs contributed 18% and 8% ΣFRs in homes and offices,
199 respectively (Figure S2, SI). The comparatively high abundance of EFRs in both offices (38%)
200 and homes, suggests their widespread use in the UK. The far greater abundance of EFRs in
201 offices could be attributable to different and greater numbers of sources in offices compared to
202 homes, and also reflect a more rapid turnover of such source items in offices – i.e. putative FR
203 sources such as foam filled office furniture and electronic and electrical equipment are more
204 frequently replaced in offices. Such rapid "turnover" of old source items containing LFRs with
205 new replacements containing EFRs, may explain the predominance of the latter in offices.

206 **Levels of FRs in indoor dust**

207 Table 2 summarises the concentrations of target FRs in UK homes and office dust.

EFRs

In contrast to air, less volatile compounds were more frequently detected in office and home dust. These include: DDC-CO, TBBPA-BDBPE and DBDPE (DF>60%) (Table 2). Of note is the very high concentration of 4,700,000 ng/g BTBPE detected in one office dust sample, which to the authors' knowledge is the highest BTBPE level reported in indoor dust to date. We are unable to explain this high concentration based on a survey of putative FR-treated items in the sampled office. TBBPA-BDBPE was the most abundant compound, comprising 87% and 71% ∑EFRs in homes and offices based on median concentrations, followed by BEH-TEBP, BTBPE, and DBDPE. TBBPA-BDBPE was also the predominant EFR detected previously in UK classroom dust, accounting for an average of 48% ΣEFRs,[12] indicating its extensive UK use. Concentrations of TBBPA-BDBPE in this study exceeded those in Belgian homes and offices[12] and USA homes[8]. In office dust, concentrations of BTBPE, BEH-TEBP, and DBDPE in this study were comparable to those in offices in Beijing, China[57] but exceeded those in Belgian offices[12]. For house dust, our concentrations were comparable to those in Belgium, New Zealand, Germany, Sweden, and Norway but lower than those found in USA and Canada.[8,10–12,15,58–60] In studies not targeting TBBPA-BDBPE; the most abundant EFRs in house dust from Norway, Germany, Sweden, USA and China were DBDPE and BEH-TEBP[8–11,15]. We observed a similar abundance of DBDPE and BEH-TEBP. Our data also represent the first report of DDC-CO in UK indoor dust at median concentrations of 5.7 and 73 ng/g in homes and offices, respectively. The contribution of *anti*-DDC-CO to ΣDDC-CO (expressed as f_{anti}) in the technical mixture is 0.65−0.75.[15] By comparison, f_{anti} values in our indoor dust samples are 0.27-0.99. This wider range is similar to previous studies of indoor dust from Canada, China and Sweden.[14,60,61] Similar to DBE-DBCH in air, plausible explanations include: isomer-specific degradation, variable environmental

behaviour arising from different physicochemical properties, as well as possible thermal isomerization during incorporation of DDC-CO into consumer products.

DBE-DBCH was detected in all indoor dust samples underlining its wide UK application. $f_{\beta\text{-DBE-DBCH}}$ in indoor dust was 0.32-2.88 (median=0.85). This median value is lower than in the commercial product. Interestingly, $f_{\beta\text{-DBE-DBCH}}$ values in indoor dust significantly exceed those in indoor air ($p<0.01$). Few studies have addressed isomer-specific aspects of DBE-DBECH. Wong et al.[63] reported the fate of DBE-DBCH in urban soil, with β-DBE-DBCH showing a slightly higher soil-air partition coefficient (K_{SA}) than α-DBE-DBCH, indicating β-DBE-DBCH to be less volatile than α-DBE-DBCH. This may provide a plausible explanation for the observed low $f_{\beta\text{-DBE-DBCH}}$ in indoor air and dust compared to the commercial formulation. Combined with the reported slightly faster degradation rate of α- compared to β-DBE-DBCH[63], this may contribute to the significantly lower $f_{\beta\text{-DBE-DBCH}}$ observed in indoor dust compared to air. The fate of DBE-DBCH isomers in the environment, the reasons for different isomeric profiles in various matrices and possible implications of such variations on exposed organisms are a research priority.

PBDEs

Each target PBDE was detected in >90% of indoor dust samples except for BDE-28 and BDE-47 (Table 2). In house dust, concentrations of ∑PBDEs were 180-370000 ng/g (median=4600 ng/g). This exceeds those reported in other countries like: Germany (36.6-1580 ng/g), Denmark (65-61524), Sweden (53-4000 ng/g), USA (920-17000 ng/g), Belgium (4-6509 ng/g), and China (132-3887 ng/g) but is comparable to Canada (170-170000 ng/g).[51,52,64–68] In our office dust samples, concentrations of ∑PBDEs were 270-110000 ng/g (median=3000 ng/g). This is comparable to the USA, Sweden and China but higher than Belgium.[51,55,67,69] Similar to previous

UK studies, BDE-209 predominated in dust, contributing 99% and 94% ΣPBDEs in homes and offices, respectively. This predominance of BDE-209 concurs with other countries in Europe and Asia, but is more marked than in North America, where greater use of Penta-BDE leads to a greater contribution from BDEs-47 and 99.[51,52,55,64–67,69] The substantially higher concentrations of BDE-209 in UK indoor dust compared to other European countries, may be attributed to the extensive UK use of Deca-BDE in upholstery fabrics and textiles (1,000-1,200 tonnes/year out of an estimated 1,500 tonnes/year in the EU for this application) to comply with the UK Furniture and Furnishing Fire Safety Regulations 1988.[70]

HBCDDs

HBCDDs were detected in all samples. ∑HBCDDs concentrations in homes were 50-110000 ng/g (median=610 ng/g) in homes, which compares closely with those previously detected in UK house dust (140-140000 ng/g)[57]. In office dust, concentrations of ∑HBCDDs were 150-6400 ng/g (median=1700 ng/g). This is also in line with previous UK data (90-6600 ng/g).[57] Our ∑HBCDDs concentrations in office and house dust exceeded those in dust from offices, apartments, stores and two schools in Sweden (17-2900 ng/g).[14] In our study, α-HBCDD was the dominant contributor to ΣHBCDD in home and office dust. The average isomer profile was 53% α-HBCDD, 29% γ-HBCDD, and 18% β-HBCDD in homes, while for offices; it was 56% α-HBCDD, 27% γ-HBCDD, and 17% β-HBCDD. This pattern differs from that in indoor air. To investigate whether the difference is statistically significant, fractional contributions of α-HBCDD and γ-HBCDD to ΣHBCDD detected in matched pairs (n=32) of indoor air and dust samples, i.e. collected from the same room at the same time were compared. Similar to a previous UK study, we found greater relative abundance of α-HBCDD in dust relative to air,

with the opposite observed for γ-HBCDD ($p<0.001$). As previously, we attribute this to a post-depositional shift from γ-HBCDD to α-HBCDD, and/or preferential degradation of γ-HBCDD in indoor dust.[57]

Relative abundance of FRs in indoor dust

Similar to indoor air, PBDEs predominated in house dust, contributing 66 % ΣFRs, while EFRs dominated in office dust, accounting for 51% ΣFRs. ΣHBCDDs contributed 9% and 17% ΣFRs in home and office dust, respectively (Figure S3).

Temporal trends in UK indoor contamination

EFRs

To our knowledge, these are the first data about concentrations of EFRs in UK indoor air. Consequently, comparison with previous studies is not possible. With respect to indoor dust however, concentrations of BTBPE and DBDPE in dust taken from homes (n=30) and offices (n=18) in the West Midlands collected between July 2006 and June 2007 exist[13]. Following log-transformation of concentrations, we conducted a t-test to compare concentrations in these two studies. For house dust, concentrations of BTBPE in our study were statistically indistinguishable to the previous study ($p>0.05$); in contrast, concentrations of DBDPE exceeded significantly ($p<0.05$) those in the earlier study. Moreover, t-test comparison revealed concentrations of BTBPE and DBDPE in our office dust samples were both significantly higher than those reported previously ($p<0.05$).[13] While based on a relatively limited number of samples, these findings suggest restrictions on LFRs have led to a concomitant increase in concentrations in UK indoor dust of DBDPE and – to a lesser extent – BTBPE.

296 *PBDEs*

297 Two previous studies have reported concentrations of PBDEs in UK indoor air. The first reported
298 concentrations of BDE-47, 99, 100, 153, and 154 in air from offices and homes using high-
299 volume active air samplers from 2001-2002[71]; while the second - conducted between September
300 2003 and November 2005 - measured BDE-28, 47, 49, 66, 85, 99, 100, 153, and 154 using
301 double-bowl passive air samplers containing a PUF disk[72]. For home air, no significant
302 difference was observed between our study and the two previous studies[71,72]. By comparison, for
303 office air, concentrations of BDE 47 and 99 were significantly lower than in previous studies
304 (ANOVA test of log transformed concentrations, $p<0.05$)[71,72]. We are aware of the potential
305 difficulties of comparing concentrations derived using different air sampler configurations. Two
306 studies that examined such difficulties are: (a) Melymuk et al. (2012), who found no major
307 differences between PBDE concentrations derived using passive air samplers and high volume
308 active samples; and (b) Abdallah and Harrad (2010), who found no significant difference
309 between indoor air concentrations of BFRs including PBDEs measured using both passive and
310 low volume active samplers. On the basis of these previous studies, we conclude the influence of
311 the different sampling methods used in the three studies compared here, should not overly
312 obscure the temporal trend.

313 Concentrations of BDE-209 in UK office dust were significantly lower ($p<0.05$) than those
314 reported in a previous study of UK offices[13]; while for UK house dust, BDE-209 concentrations
315 were comparable ($p>0.05$) to those reported previously[13], perhaps indicating more rapid removal
316 of "legacy" PBDEs in offices than homes. No significant temporal differences were found for
317 other PBDEs in both home and office dust. We attribute the lack of a decline in BDEs- 47 and 99
318 in dust (in contrast to air) to the different sample populations for air and dust.

HBCDDs

We compared our data for HBCDDs in indoor air with those in the previous UK study[57] by independent t-test. In domestic air, no significant differences were detected; in contrast, concentrations of γ-HBCDD were significantly lower in office air in our study ($p<0.001$) (α–HBCDD and β–HBCDD were not compared as DFs were <60%). This may possibly indicate replacement of HBCDDs by EFRs such as DBE-DBCH in expanded polystyrene for building insulation[14]. For indoor dust, our concentrations of γ-HBCDD in house dust were significantly lower ($p<0.001$) than in the previous study[57] but not for other diastereomers and ΣHBCDDs. No significant differences were observed for office dust.

Comparisons between indoor microenvironments

Previous studies of both air and dust revealed differences in concentrations of FRs between offices and homes[13,67,71,72]. Such differences are likely due to the different types and abundance of FR sources in these two microenvironment categories. We therefore examined our data for such differences.

Indoor air

We compared concentrations in home and office air using an independent t-test. For EFRs, DBE-DBCH, PBBz and EH-TBB were significantly higher in offices than homes ($p<0.001$ for DBE-DBCH, $p<0.05$ for PBBz and EH-TBB), with no significant differences between homes and offices detected for other EFRs. For PBDEs, concentrations of BDE-209 were significantly higher in homes than offices ($p<0.005$); but no differences were found for other congeners. In

contrast, previous studies in West Midlands indoor air focusing on tri- to hexa-BDEs found concentrations in offices to exceed those in homes ($p<0.05$).[71,72] Finally, for HBCDDs, concentrations of γ-HBCDD were significantly higher ($p<0.005$) in homes than offices. (α–HBCDD and β–HBCDD were not compared as their DFs were <60%).

Indoor dust

For indoor dust, statistical analysis revealed concentrations of DBE-DBCH, EH-TBB, BEH-TEBP, BTBPE, DDC-CO and DBDPE in offices exceeded significantly those in homes. No significant differences between offices and homes were found for other EFRs.

In contrast to our observations for air, BDE-209 concentrations in homes and offices were comparable ($p>0.05$), while for BDE-47 and BDE-99, concentrations in offices exceeded significantly ($p<0.001$) those in homes. This result concurs with previous studies of PBDEs in Belgian and UK home and office dust[13,67]. We attribute the differences between air and dust (e.g. BDE-209 higher in homes than offices for air but dust) to the larger number of dust samples collected.

For HBCDDs, no significant differences were detected between concentrations of ΣHBCDDs in dust from homes and offices ($p>0.05$); consistent with a previous study[57].

Correlations between FRs in the studied microenvironments

To investigate potential common sources of our FRs. Pearson correlation analysis was applied to assess relationships between the target compounds (Table S5 and 6). α-DBE-DBCH concentrations correlated significantly with those of β-DBE-DBCH in both air and dust samples ($p<0.001$) with similar findings observed for HBCDD diastereomers. Significant correlations

between concentrations of tetra- to hexa-BDEs were observed in indoor air and dust ($p<0.05$), with BDE-183 correlated with BDE-47 ($p<0.005$), BDE-100 ($p<0.05$), BDE-153 ($p<0.01$) and BDE-154 ($p<0.001$) in indoor dust. This probably reflects the presence of these congeners in Penta-BDE and Octa-BDE.

For EFRs, PBBz was correlated significantly with PBEB, TBP-DPTE and HBB in indoor air and dust. HBB also correlated with PBEB and TBP-DPTE in indoor air ($p<0.001$), with HBB and PBBz correlated with BDE-28, 47 and 99 in air and dust ($p<0.05$). While some of these observed correlations are hard to rationalise and may have occurred by chance; those between PBEB, HBB and PBBz may originate from a common source resulting from thermal degradation of polymeric FRs. Conditions that may favour such formation may be encountered during the process of incorporating these FRs into goods – i.e. the elevated temperatures experienced by FRs when incorporated into molten polymers.[74–76]

Correlations between FR concentrations in air and dust

If semi-volatile organic compounds (SVOCs) partitioning between the gaseous and particulate phases have reached equilibrium under ideal conditions, their concentrations in air and dust should correlate.[77] To investigate this hypothesis, Pearson correlation analysis was conducted to investigate the relationship between FR concentrations in matched air and dust samples (n=30, Table S7). Significant correlations between concentrations of EFRs in air and dust were observed ($p<0.005$), especially for the more volatile EFRs, e.g. DBE-DBCH and PBT. Moreover, concentrations of BDE-28 and 47 in air and dust were also significantly correlated ($p<0.05$). The partition coefficient between dust and air is expressed as K_{DA} ($K_{DA}= C_{dust}/C_{air}$, where C_{dust} and C_{air} are the concentrations of FR in dust and air, respectively). Median values of Log K_{DA} in

383 homes and offices were linearly associated with K_{OA} values of the studied FRs (Figure S4),
384 suggesting thermodynamic equilibrium to exist between air and dust for most target FRs. Similar
385 relationships were reported by Cequier et al.[41] for PFRs and PBDEs in Norwegian homes and
386 classrooms who concluded knowledge of concentrations of FRs in either air or dust permits
387 prediction of their levels in the other phase given the K_{OA} of the compound in question. [41]

388 No correlation between Log K_{DA} and K_{OA} of HBCDD diastereomers was found. This is
389 consistent with the previously observed post-depositional transformation in dust of
390 HBCDDs.[57,78]

391 **Exposure to FRs via inhalation and dust ingestion**

392 Human exposure to FRs via inhalation and dust ingestion was estimated based on concentrations
393 reported here. The algorithms and assumptions applied to estimate exposure via different routes
394 are provided in SI. These data are important – especially for the EFRs – as they facilitate: (a)
395 evaluation of the relative importance of inhalation as opposed to dust ingestion (and dietary
396 exposure once such data are available) for different chemicals, and (b) future risk assessment by
397 comparison of exposure with health-based limit values once set. Median estimated exposure for
398 toddlers via air inhalation to ∑EFRs, ∑PBDEs and ∑HBCDDs was 0.66, 0.43 and 0.14 ng/day,
399 respectively. For adults, estimated exposure via inhalation to ∑EFRs, ∑PBDEs and ∑HBCDDs
400 was 4.3, 2.0 and 2.1 ng/day, respectively. Our estimated inhalation exposures to ∑tri-hexa BDEs
401 (Table 3) were comparable to those reported previously for UK toddlers and adults (0.16 and
402 0.82 ng/day respectively)[72]. There are no previous estimates of human exposure to BDE-209 via
403 inhalation in the UK. For ΣHBCDDs, Abdallah et al.[57] reported median daily intakes of 0.8 and
404 3.9 ng/day for UK toddlers and adults, slightly exceeding our estimates (Table 3).

405 The main contributors to adult inhalation exposures were: α-DBE-DBCH, β-DBE-DBCH, BDE-
406 209 and γ-HBCDD, contributing 21%, 14%, 17% and 24% to the median ΣFRs exposure,
407 respectively. Similar findings were observed for toddlers (Figure 1 and Figure S5 and 6).

408 Estimates of "typical" exposure for toddlers (i.e. dust contaminated at the median concentration
409 ingested at the mean dust ingestion rate) to ∑EFRs, ∑PBDEs and ∑HBCDDs were 38, 280 and
410 25 ng/day, respectively. For adults, "typical" exposures to ∑EFRs, ∑PBDEs and ∑HBCDDs
411 were 27, 100 and 15 ng/day, respectively. Harrad et al.[13] reported "typical" exposure of toddlers
412 and adults to ∑PBDEs via dust ingestion to be 234.3 and 612.6 ng/day respectively, which in
413 both instances exceeds our exposure estimates (Table 3). A previous study reported UK exposure
414 to ∑HBCDDs via dust ingestion to be 86.9 and 32.5 ng/day for toddlers and adults respectively,
415 which also exceeds our current estimates (Table 3)[57]. For EFRs, our "typical" exposure estimates
416 for UK adults and toddlers via dust ingestion exceed substantially those reported in a previous
417 study[12] (Table 3). While this suggests UK exposure to LFRs via dust ingestion is decreasing, a
418 substantial increase in exposure to EFRs is a potential cause for concern.

419 Under our "typical" exposure scenario, dust ingestion is a more significant contributor to human
420 exposure to ∑EFRs, ∑PBDEs and ∑HBCDDs than air inhalation (Table 3). This is similar to
421 the findings of previous studies on PBDEs and HBCDDs[57,72]. For toddlers' intake of FRs, dust
422 ingestion was more important than air inhalation for all target compounds. However, for FRs
423 with relatively high vapor pressures (e.g. DBE-DBCH and BDE-28), inhalation contributes more
424 to UK adult exposure than dust ingestion (Table 3).

425 **Acknowledgment**

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Supporting Information

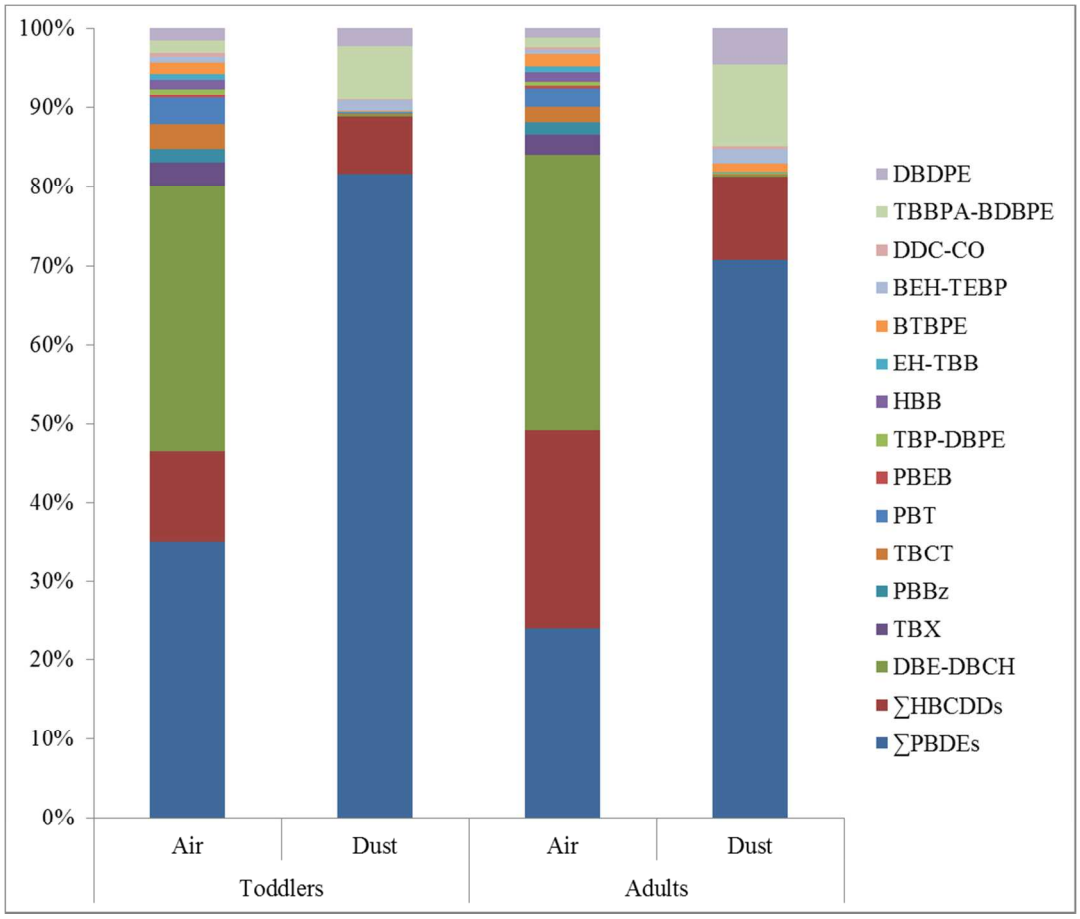
Full details of the analytical protocols, QA/QC measurements and human exposure assessment models are provided as supporting information. This material is available free of charge via the Internet at http://pubs.acs.org.

433

434 # Figures

435 **Figure 1.** Relative contribution (expressed as %) of different target FRs to the overall daily

436 exposure (ng/day) of UK toddlers and adults via inhalation and dust ingestion.



437

Tables

Table 1. Descriptive Statistics for Concentrations (pg/m^3) of target FRs in UK indoor air

Statistical Parameter	Homes					Offices				
	This study, n=15				UK previous studies	This study, n=20				UK previous studies
	DF	Mean	Median	Range	Range	DF	Mean	Median	Range	Range
α-DBE-DBCH	100%	99	64	17-350	--	100%	180	160	74-440	--
β-DBE-DBCH	100%	74	45	13-250	--	100%	140	120	41-300	--
TBX	100%	31	9.7	1.6-190	--	100%	16	14	2.6-38	--
PBBz	93%	6.6	5.3	<0.10-22	--	100%	16	11	3.1-47	--
TBCT	60%	22	9.9	<0.10-240	--	65%	1.6	<0.10	<0.10-11	--
PBT	100%	17	11	2.3-63	--	65%	15	4.7	<0.10-200	--
PBEB	100%	1.6	1.3	0.41-5.4	--	100%	4.2	1.7	0.31-35	--
TBP-DBPE	93%	3.5	2	<0.40-14	--	85%	18	1.9	<0.40-280	--
HBB	73%	11	4.2	<0.20-91	--	85%	19	9.4	<0.20-170	--
EH-TBB	100%	4.8	2	0.05-44	--	100%	22	5.3	0.67-240	--
BTBPE	73%	11	5	<1.0-50	--	100%	32	11	0.7-220	--
BEH-TEBP	93%	10	2.1	<0.10-130	--	90%	2.2	1.4	<0.10-11	--
***syn*-DDC-CO**	7%	<2.0	<2.0	<2.0-4.6	--	5%	1.3	<2.0	<2.0-7.7	--
***anti*-DDC-CO**	20%	2.2	<1.2	<1.2-20	--	5%	1.8	<1.2	<1.2-24	--
TBBPA-BDBPE	20%	13	<10	<10-87	--	5%	7.3	<10	<10-50	--
DBDPE	40%	26	<10	<10-97	--	5%	7.5	<10	<10-54	--
BDE28	100%	22	1.2	0.21-310	<dl-60.8 [b]	100%	4.3	2.7	0.81-13	<dl-43.5 [b]
BDE47	100%	120	13	0.15-1700	45-1330 [a]; 1.9-106.9 [b]	100%	44	6	0.15-380	58-7140 [a]; 4.0-567.6 [b]
BDE100	87%	44	1.5	<0.10-600	2.6-82 [a]; <dl-26.5 [b]	85%	3	1.5	<0.10-17	4.1-1450 [a]; <dl-142.4 [b]
BDE99	100%	130	12	0.05-1700	8.7-209 [a]; <dl-80.4 [b]	100%	9.2	7.9	1.2-42	9.0-6510 [a]; 3.9-633.5 [b]
BDE154	53%	14	1.2	<0.50-180	<1.0-6.0 [a]; <dl-16.5 [b]	40%	0.78	<0.50	<0.50-6	<1.0-228 [a]; <dl-12.8 [b]
BDE153	67%	24	1.8	<0.4-180	<1.0-6.1 [a]; <dl-20.5 [b]	55%	0.6	<0.4	<0.4-3.6	<1.0-181 [a]; <dl-7.0 [b]
BDE183	27%	2.8	<1.0	<1.0-12	--	10%	<1.0	<1.0	<1.0-3.8	--
BDE209	100%	660	170	23-3800	--	100%	74	26	2.3-350	--
α–HBCDD	40%	43	<2.6	<2.6-400	14-430 [c]	59%	8.8	5.4	<2.6-31	18-87 [c]
β–HBCDD	47%	17	<2.2	<2.2-160	5-54 [c]	53%	5.2	<2.2	<2.2-15	14-34 [c]
γ–HBCDD	100%	270	110	16-1400	39-710 [c]	100%	55	34	3.1-320	43-370 [c]
ΣHBCDDs	--	320	110	19-1500	67-1300 [c]	--	69	41	5.5-360	70-460 [c]

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446

447 **Table 2.** Descriptive Statistics for Concentrations (ng/g) of target FRs in UK indoor dust

Statistical Parameter	Homes					Offices				
	This study, n=45				UK previous studies	This study, n=47				UK previous studies
	DF	Mean	Median	Range	Range	DF	Mean	Median	Range	Range
α-DBE-DBCH	100%	9.4	5.9	1.4-52	--	100%	23	15	2.5-130	--
β-DBE-DBCH	100%	12	6.2	1.5-77	--	100%	18	13	2.7-120	--
TBX	80%	18	1.4	<0.010-410	--	98%	3.2	2.1	<0.010-19	--
PBBz	87%	3.3	2.2	<0.010-12	--	91%	4.5	3.3	<0.010-23	--
TBCT	40%	21	<0.010	<0.010-300	--	67%	11	3.4	<0.010-68	--
PBT	67%	7.1	1.8	<0.010-90	--	87%	6	2.5	<0.010-59	--
PBEB	87%	2.3	0.78	<0.010-21	--	100%	2	1.4	0.36-10	--
TBP-DBPE	84%	6.6	1.8	<0.050-47	--	98%	24	4.7	<0.050-370	--
HBB	75%	1.8	<0.030	<0.030-12	--	91%	14	9.9	<0.030-84	--
EH-TBB	94%	21	10	<0.010-85	--	91%	120	31	<0.010-2000	--
BTBPE	100%	14	5.6	0.01-110	<dl-1900 [a]	100%	100000	160	0.019-4700000	<dl-40 [a]
BEH-TEBP	100%	240	65	16-3500	--	100%	1000	160	54-25000	--
***syn*-DDC-CO**	63%	3.6	0.77	<0.26-28	--	98%	60	11	<0.26-640	--
***anti*-DDC-CO**	84%	21	4.9	<0.15-170	--	98%	210	62	<0.15-2100	--
TBBPA-BDBPE	100%	5800	1000	71-49000	--	100%	3400	2300	310-14000	--
DBDPE	60%	240	41	<1.2-2300	<dl-3400 [a]	96%	1600	440	<1.2-17000	<dl-860 [a]
BDE28	57%	1.9	0.16	<0.03-15	<dl-2.1 [a]	82%	3.9	2.6	<0.03-22	<dl-11 [a]
BDE47	77%	14	13	<0.04-50	1.2-58 [a]	100%	83	37	7.1-660	2.6-380 [a]
BDE100	100%	4.2	3	0.75-16	<dl-17 [a]	100%	18	12	1.9-120	<dl-79
BDE99	100%	31	22	5-92	2.8-180 [a]	100%	100	77	15-480	4.2-490 [a]
BDE154	94%	2	1.2	<0.06-9.3	<dl-16 [a]	100%	7.7	3.9	0.8-68	<dl-38 [a]
BDE153	100%	4.8	3	0.025-24	<dl-110 [a]	100%	28	9.2	0.025-190	<dl-99 [a]
BDE183	90%	7.4	3.5	<0.13-51	<dl-550 [a]	100%	29	9.8	0.065-220	<dl-24 [a]
BDE209	100%	34000	4500	160-370000	<dl-2200000 [a]	100%	9100	2700	200-110000	620-280000 [a]
α–HBCDD	100%	2300	320	21-28000	22-66000 [b]	100%	1100	980	100-2800	15-2900 [b]
β–HBCDD	100%	1100	85	6.1-12000	9-26000 [b]	100%	300	330	22-590	11-1300 [b]
γ–HBCDD	100%	4900	93	23-71000	70-75000 [b]	100%	630	350	31-3700	36-3700 [b]
ΣHBCDDs	--	8300	610	50-110000	140-140000 [b]	--	2000	1700	150-6400	90-6600 [b]

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452 **Table 3.** Estimates of exposure (ng/day) of UK Adults and Toddlers to FRs via air and dust, and
453 relative significance (%) of each pathway under a typical exposure scenario [a]
454

Compounds	Intake (ng/day)			
	Toddlers		Adults	
	Air	Dust	Air	Dust
∑tri-hepta BDEs	0.11	10	0.6	2.1
BDE209	0.32	270	1.4	100
∑HBCDDs	0.14	25	2.1	15
∑EFRs	0.66	38	4.3	27
α–DBE-DBCH	0.24	0.31	1.7	0.16
β–DBE-DBCH	0.17	0.44	1.2	0.18
TBX	0.037	0.065	0.21	0.027
PBBz	0.02	0.11	0.13	0.047
TBCT	0.038	0.42	0.16	0.16
PBT	0.042	0.15	0.2	0.054
PBEB	0.005	0.017	0.028	0.009
TBP-DBPE	0.0075	0.058	0.039	0.031
HBB	0.016	0.083	0.11	0.07
EH-TBB	0.0075	0.35	0.053	0.19
BTBPE	0.019	0.31	0.13	1.5
BEH-TEBP	0.008	4.7	0.039	2.6
syn -DDC-CO	0.0038	0.014	0.02	0.058
anti-DDC-CO	0.0023	0.46	0.012	0.52
TBBPA-BDBPE	0.019	23	0.1	15
DBDPE	0.019	7.8	0.1	6.5

455 [a] typical exposure scenario denotes adults and toddlers assumed to inhale air and ingest dust contaminated at the
456 median concentration at the average ingestion rate (20 mg/day and 50 mg/day for adults and toddlers respectively)

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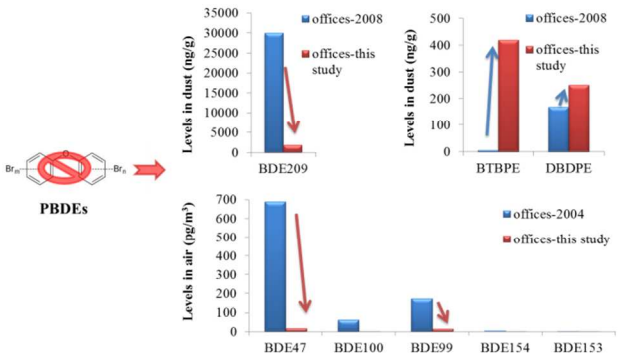
685 

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